

SPECIFICATION

LIQUID CRYSTAL SEALING AGENT AND LIQUID CRYSTAL DISPLAY CELL UTILIZING THE SAME

Technical Field

The present invention relates to a liquid crystal sealing agent used for bonding TFT substrates and CF substrates, and for enclosing liquid crystals in the inside, and a liquid crystal display cell utilizing the same.

Background Art

In recent years, liquid crystal display cells are undergoing a wide spread of the application to large size display screens such as televisions, and are increasingly demanded for various purposes. These liquid crystal display cells are produced by enclosing liquid crystals between an upper glass substrate and a lower glass substrate, which are fixed with a resin. Furthermore, recently, a liquid crystal dropping technique in which liquid crystal is dropped within a weir formed from a resin, and then bonding is carried out to cure the resin, has also been in practical use. In these production methods, the upper and lower substrates are bonded, and also liquid crystals are enclosed, by means of a liquid crystal sealing agent which is brought to direct contact with the liquid crystals. Therefore, the liquid crystal sealing agent is required to have a property of not contaminating liquid crystals, even if brought to contact with the liquid crystals. At the same time, the liquid crystal sealing agent is required to be rapidly curable, while having a long pot life, from the viewpoint of the production line tact. The long-term reliability of produced panels is also an important item, and in particular, moisture resistance reliability also represents another property that is required from a sealing agent.

There have been many suggestions for a sealing agent having these properties (Patent Document 1, Patent Document 2, Patent Document 3, Patent Document 4, and Patent Document 5), but a sealing agent having substantially all of the properties still have not been found. Moreover, in the current liquid crystal panel market where high

definition is being sought for, further enhancement of the properties of the sealing agent is demanded, and thus there is a problem in that the properties of the sealing agent do not follow the progress.

[Patent Document 1]	Japanese Patent No. 2754004
[Patent Document 2]	Japanese Patent No. 3583326
[Patent Document 3]	JP-A No. 2001-89743
[Patent Document 4]	JP-A No. 10-273644
[Patent Document 5]	JP-A No. 2004-61925

Disclosure of the Invention

Problems to be Solved by the Invention

The present invention is to provide a liquid crystal sealing agent having low contaminability to liquid crystals throughout the production process, excellent workability in the coating of substrates, excellent pot life, and excellent moisture resistance reliability.

Means for Solving the Problems

The inventors of the present invention have devotedly and repeatedly carried out research in order to solve the above-described problems, and as a result, they conceived of using an aromatic hydrazide compound and an aliphatic hydrazide compound in combination, as thermosetting components, thus completing the present invention.

Specifically, the present invention relates to the following (1) to (9).

(1) A liquid crystal sealing agent comprising (a) an epoxy resin, (b) an aromatic hydrazide compound, and (c) an aliphatic hydrazide compound.

(2) The liquid crystal sealing agent according to (1) above, wherein the component (b) is an aromatic dihydrazide, and the component (c) is an aliphatic dihydrazide.

(3) The liquid crystal sealing agent according to (1) or (2) above, further comprising (d) a photocurable resin, and (e) a photoradical polymerization initiator, in addition to the component (a), component (b) and component (c).

(4) The liquid crystal sealing agent according to (3) above, wherein the

component (d) is an acrylic resin.

(5) The liquid crystal sealing agent according to (3) or (4) above, wherein the component (d) is an epoxy acrylate resin.

(6) The liquid crystal sealing agent according to any one of (1) to (5) above, further comprising (f) a silane coupling agent.

(7) The liquid crystal sealing agent according to any one of (1) to (6) above, further comprising (g) an inorganic filler having an average particle size of 3 μm or less.

(8) The liquid crystal sealing agent according to any one of (1) to (7) above, having a viscosity of 250 Pa·s or less.

(9) A liquid crystal display cell sealed with a cured product obtainable by curing the liquid crystal sealing agent according to any one of (1) to (8) above.

Best Mode for Carrying Out the Invention

Hereinafter, the present invention will be described in detail.

The epoxy resin (a) that can be used in the present invention is not particularly limited, but an epoxy resin having bifunctionality or higher functionality is preferred, and examples thereof include bisphenol A type epoxy resins, bisphenol F type epoxy resins, bisphenol S type epoxy resins, phenol-novolac type epoxy resins, cresol-novolac type epoxy resins, bisphenol A-novolac type epoxy resins, bisphenol F-novolac type epoxy resins, alicyclic epoxy resins, aliphatic chain-like epoxy resins, glycidyl ester type epoxy resins, glycidylamine type epoxy resins, hydantoin type epoxy resins, isocyanurate type epoxy resins, and phenol-novolac type epoxy resins having a triphenolmethane skeleton; as well as diglycidyl etherification products of bifunctional phenols, diglycidyl etherification products of bifunctional alcohols, and halogenation products thereof, hydrogenation products thereof, and the like. Among these, preferred from the viewpoint of liquid crystal contamination properties are bisphenol type epoxy resins and novolac type epoxy resins.

The amount of hydrolyzable chloride in the epoxy resin used in the present invention is 600 ppm or less, and preferably 300 ppm or less. If the amount of hydrolyzable chloride is greater than 600 ppm, the contamination properties of the liquid

crystal sealing agent against liquid crystals pose a problem. The amount of hydrolyzable chloride can be determined by, for example, dissolving about 0.5 g of epoxy resin in 20 ml of dioxane, refluxing the solution for 30 minutes in 5 ml of a 1 N KOH/ethanol solution, and then titrating the product with a 0.01 N silver nitrate solution. The content of such epoxy resin (a) in the liquid crystal sealing agent is about 5 to 50% by weight.

Furthermore, the component (b) that can be used in the present invention is not particularly limited as long as it is an aromatic hydrazide compound, and for example, there may be mentioned salicylic acid hydrazide, benzoic acid hydrazide, 1-naphthoic acid hydrazide, terephthalic acid dihydrazide, isophthalic acid dihydrazide, 2,6-naphthoic acid dihydrazide, 2,6-pyridine dihydrazide, 1,2,4-benzene trihydrazide, 1,4,5,8-naphthoic acid tetrahydrazide, pyromellitic acid tetrahydrazide, and the like. According to the present invention, preferred from the viewpoint of the balance between curing reactivity and curing latency are bifunctional aromatic dihydrazides, and particularly preferably, isophthalic acid dihydrazide may be mentioned.

The component (c) that can be used in the present invention is not particularly limited as long as it is an aliphatic hydrazide compound, and for example, there may be mentioned formhydrazide, acetohydrazide, propionic acid hydrazide, oxalic acid dihydrazide, malonic acid dihydrazide, succinic acid dihydrazide, glutaric acid dihydrazide, adipic acid dihydrazide, pimelic acid dihydrazide, 1,4-cyclohexane dihydrazide, tartaric acid dihydrazide, malic acid dihydrazide, iminodiacetic acid dihydrazide, N,N'-hexamethylene bis-semicarbazide, citric acid trihydrazide, nitriloacetic acid trihydrazide, cyclohexanetricarboxylic acid trihydrazide, dihydrazides having a valinehydantoin skeleton such as 1,3-bis(hydrazinocarbonoethyl)-5-isopropylhydantoin, and the like. According to the present invention, preferred from the viewpoint of the balance between curing reactivity and curing latency are bifunctional aliphatic dihydrazides, and particularly preferably, adipic acid dihydrazide may be mentioned.

Since the particle size of these hydrazide compounds may become a cause of defect if too large, such that during the production of a liquid crystal cell having a narrow gap, the formation of gap cannot be successfully achieved upon bonding of the upper and

lower glass substrates, the average particle size is preferably 3 μm or less, and more preferably 2 μm or less. Likewise, the maximum particle size is preferably 8 μm or less, and more preferably 5 μm or less. This particle size is measured using a laser diffraction/scattering particle size distribution measuring instrument (dry type) (manufactured by Seishin Enterprise Co., Ltd.; LMS-30).

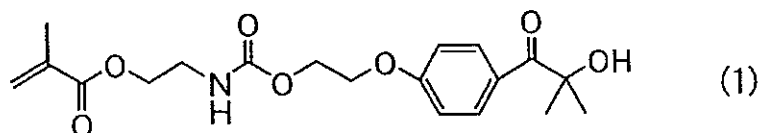
The content of the aromatic hydrazide compound of component (b) in the liquid crystal sealing agent of the present invention is preferably 0.20 to 0.80 equivalents, particularly preferably 0.4 to 0.6 equivalents, based on the epoxy equivalent of epoxy groups of the epoxy resin of component (a). Furthermore, the content of the aliphatic hydrazide compound of component (c) is preferably 0.20 to 0.80 equivalents, and particularly preferably 0.4 to 0.6 equivalents, based on the epoxy equivalent of epoxy groups of the epoxy resin of component (a).

The photocurable resin (d) that can be used in the present invention is not particularly limited as long as it has low elutability to liquid crystals, but there may be mentioned compounds having an acryloyl group as a functional group (acrylic resins), such as urethane acrylates, (meth)acrylic esters and epoxy (meth)acrylates, and the like. Specific examples thereof include benzyl methacrylate, cyclohexyl methacrylate, glycerol dimethacrylate, glycerol triacrylate, EO-modified glycerol triacrylate, pentaerythritol acrylate, trimethylolpropane triacrylate, tris(acryloxyethyl) isocyanurate, dipentaerythritol hexaacrylate, phloroglucinol triacrylate, and the like. Among these, from the aspect of liquid crystal contamination properties, epoxy (meth)acrylate resins are particularly preferred. This epoxy acrylate resin or epoxy methacrylate resin can be obtained by esterifying an epoxy resin having at least two epoxy groups in the molecule, with acrylic acid or methacrylic acid. This synthesis can be performed by a generally known method. For example, an epoxy resin is esterified with acrylic acid or methacrylic acid at a predetermined equivalent ratio by adding a catalyst (for example, benzyldimethylamine, triethylamine, benzyltrimethylammonium chloride, triphenylphosphine, triphenylstibine, and the like) and a polymerization inhibitor (for example, methoquinone, hydroquinone, methylhydroquinone, phenothiazine, dibutylhydroxytoluene, and the like), at 80 to 110 $^{\circ}\text{C}$ for example. As the epoxy resin

having at least two epoxy groups in the molecule, for example, there may be mentioned bisphenol A type epoxy resins, alkyl-substituted bisphenol A type epoxy resins, alkylene oxide-added bisphenol A type epoxy resins, bisphenol F type epoxy resins, alkyl-substituted bisphenol F type epoxy resins, alkylene oxide-added bisphenol F type epoxy resins, bisphenol S type epoxy resins, alkyl-substituted bisphenol S type epoxy resins, alkylene oxide-added bisphenol S type epoxy resins, phenol-novolac type epoxy resins, cresol-novolac type epoxy resins, biphenyl type epoxy resins, naphthalene type epoxy resins, glycidylamine type epoxy resins, dicyclopentadiene type epoxy resins, silicone-modified epoxy resins, urethane-modified epoxy resins, rubber-modified epoxy resins, and the like. Bisphenol A type epoxy resins, alkyl-substituted bisphenol A type epoxy resins, alkylene oxide-added bisphenol A type epoxy resins, bisphenol F type epoxy resins, alkyl-substituted bisphenol F type epoxy resins, alkylene oxide-added bisphenol F type epoxy resins, bisphenol S type epoxy resins, alkyl-substituted bisphenol S type epoxy resins, and alkylene oxide-added bisphenol S type epoxy resins are preferred.

According to the present invention, the content of the photocurable resin (d) in the liquid crystal sealing agent is about 20 to 80 % by weight.

The photoradical polymerization initiator (e) that can be used in the present invention is not particularly limited as long as it is a radical type initiator, and for example, there may be mentioned benzyl dimethyl ketal, 1-hydroxycyclohexyl phenyl ketone, diethylthioxanthone, benzophenone, 2-ethylanthraquinone, 2-hydroxy-2-methylpropiophenone, 2-methyl-[4-(methylthio)phenyl]-2-morpholino-1-propane, 2,4,6-trimethylbenzoyldiphenylphosphine oxide, and the like. Furthermore, it is also possible to attain even lower liquid crystal contaminability, if a photoradical polymerization initiator having both a radical polymerizable group and a radical generating group in one molecule as represented by formula (1) is used.



The mixing ratio of the component (e) relative to the component (d) in the liquid crystal sealing agent of the present invention, is preferably 0.01 to 5 parts by weight, and particularly preferably 0.1 to 3 parts by weight, relative to 100 parts by weight of the component (d). If the amount of the radical generating type photoradical polymerization initiator is smaller than 0.01 parts by weight, the photocuring reaction does not occur sufficiently, whereas if the amount is greater than 5 parts by weight, the amount of the initiator becomes too large, and there occur problems of contamination of liquid crystals by the initiator, or deterioration of the properties of cured resin.

In order to enhance the adhesive strength, it is preferable that the liquid crystal sealing agent of the present invention contains a silane coupling agent (f). Examples of the silane coupling agent include silane coupling agents such as 3-glycidoxypropyltrimethoxysilane, 3-glycidoxypropylmethyldimethoxysilane, 3-glycidoxypropylmethyldimethoxysilane, 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, N-phenyl-γ-aminopropyltrimethoxysilane, N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane, N-(2-aminoethyl)-3-aminopropylmethyltrimethoxysilane, 3-aminopropyltriethoxysilane, 3-mercaptopropyltrimethoxysilane, vinyltrimethoxysilane, N-(2-(vinylbenzylamino)ethyl)-3-aminopropyltrimethoxysilane hydrochloride, 3-methacryloxypropyltrimethoxysilane, 3-chloropropylmethyldimethoxysilane, and 3-chloropropyltrimethoxysilane. These silane coupling agents may be used as mixtures of two or more species. Among these, in order to obtain better adhesive strength, it is preferable that the silane coupling agent be a silane coupling agent having an amino group. Use of the silane coupling agent leads to an enhancement of the adhesive strength, and thus a liquid crystal sealing agent having excellent moisture resistance

reliability is obtained. The content of such silane coupling agent (f) in the liquid crystal sealing agent is about 0.05 to 3 % by weight.

As the inorganic filler (g) that can be used in the present invention, fused silica, crystalline silica, silicon carbide, silicon nitride, boron nitride, calcium carbonate, magnesium carbonate, barium sulfate, calcium sulfate, mica, talc, clay, alumina, magnesium oxide, zirconium oxide, aluminum hydroxide, magnesium hydroxide, calcium silicate, aluminum silicate, lithium aluminum silicate, zirconium silicate, barium titanate, glass fiber, carbon fiber, molybdenum disulfide, asbestos and the like may be mentioned, and fused silica, crystalline silica, silicon nitride, boron nitride, calcium carbonate, barium sulfate, calcium sulfate, mica, talc, clay, alumina, aluminum hydroxide, calcium silicate and aluminum silicate are preferred, with fused silica, crystalline silica, alumina and talc being more preferred. These inorganic fillers may be used as mixtures of two or more species. Since the particle size may become a cause of defect if too large, such that during the production of a liquid crystal cell having a narrow gap, the formation of gap cannot be successfully achieved upon bonding of the upper and lower glass substrates, the average particle size is preferably 3 μm or less, and more preferably 2 μm or less. This particle size is measured using a laser diffraction/scattering particle size distribution measuring instrument (dry type) (manufactured by Seishin Enterprise Co., Ltd.; LMS-30).

The content of the inorganic filler (g) that can be used in the present invention in the liquid crystal sealing agent is usually 5 to 40 % by weight, and preferably 15 to 30 % by weight. If the content of the inorganic filler is lower than 5 % by weight, the adhesive strength to the glass substrate is decreased, and the moisture resistance reliability is deteriorated. Thus, the decrease of the adhesive strength after absorption of moisture may be increased. Also, if the content of the inorganic filler is greater than 40 % by weight, since the filler content is too large, the liquid crystal sealing agent may become hard to crush, and it may become impossible to form the gap of a liquid crystal cell.

The liquid crystal sealing agent according to the present invention may further have additives such as an organic solvent, organic fillers, pigments, a leveling agent and

a defoaming agent incorporated therein, if necessary.

The viscosity of the liquid crystal sealing agent according to the present invention is preferably 250 Pa·s or less. In the case of having a viscosity equal to or greater than 250 Pa·s, the liquid crystal sealing agent is deteriorated in the easiness in handling such as dispensability. Further, in the case of having a viscosity of 250 Pa·s or less, the liquid crystal sealing agent is possibly applicable to a seal coating method such as screen printing, and exerts great influence on the panel productivity.

In order to obtain the liquid crystal sealing agent of the present invention, first, component (d), component (e) and component (f) are dissolved and mixed with component (a), as necessary. Subsequently, to this mixture, component (g), as well as component (b), component (c), and predetermined amounts of additives such as an organic filler, a defoaming agent, a leveling agent and the like according to necessity are added, and the resulting mixture is uniformly mixed by a known mixing apparatus such as, for example, a triple roll mill, a sand mill or a ball mill. Thereby, the liquid crystal sealing agent of the present invention can be produced.

The liquid crystal display cell of the present invention is formed such that a pair of substrates having predetermined electrodes formed on the substrates are arranged to face each other with a predetermined gap therebetween, and the periphery is sealed with the liquid crystal sealing agent, with liquid crystals being enclosed within the gap. The type of the liquid crystal to be enclosed is not particularly limited. Here, the substrates are constituted of a combination of substrates made of glass, quartz, plastic, silicone or the like, at least one of them having light transmissibility. As for the method for production thereof, for example, in the case of liquid crystal injection method, a spacer (a gap controlling material) such as glass fiber is added to the liquid crystal sealing agent of the present invention, and then the liquid crystal sealing agent is coated on one of the pair of substrates using a dispenser or the like. At this time, one or two injection inlets are provided open for injecting liquid crystals. Then, the other glass substrate is superimposed thereon, such that a gap is provided. After the formation of gap, the assembly is cured at 90 to 130 °C for 1 to 2 hours to manufacture a blank cell, liquid crystals are injected through the injection inlets, and then the injection inlets are sealed

with a hole-sealing agent (a UV-curable resin). Thus, a liquid crystal display cell can be obtained.

Further, in the case of using a liquid crystal dropping method, a spacer (a gap controlling material) such as glass fiber is added to the liquid crystal sealing agent of the present invention, and then the liquid crystal sealing agent is coated such that a weir is formed on one of the pair of substrates using a dispenser or the like. Then, liquid crystal is dropped on the inner side of the weir of the liquid crystal sealing agent, and the other glass substrate is superimposed thereon in vacuo, such that a gap is provided. After the formation of gap, the liquid crystal sealed part is irradiated with ultraviolet radiation using an ultraviolet irradiator to photocure the seal. The ultraviolet irradiance level is preferably from 500 to 6000 mJ/cm², and more preferably from 1000 to 4000 mJ/cm². Thereafter, the assembly is cured at 90 to 130°C for 1 to 2 hours, and thereby the liquid crystal display cell of the present invention can be obtained. The liquid crystal display cell of the present invention thus obtained has no defects in display due to liquid crystal contamination, and has excellent adhesiveness and moisture resistance reliability. As the spacer, for example, glass fiber, silica beads, polymer beads and the like may be mentioned. The diameter may vary with the purposes, but is usually 2 to 8 μm, and preferably 4 to 7 μm. The amount of use thereof is usually about 0.1 to 4 parts by weight, preferably 0.5 to 2 parts by weight, and more preferably 0.9 to 1.5 parts by weight, relative to 100 parts by weight of the liquid crystal sealing agent of the present invention.

EXAMPLES

Hereinafter, the present invention will be described in more detail by way of Examples. Additionally, the viscosity of the liquid crystal sealing agent was measured with an R type viscometer (manufactured by Toki Sangyo Co., Ltd.).

Synthesis Example 1 Synthesis of photoradical polymerization initiator represented by above formula (1)

155 g of 2-isocyanatoethyl methacrylate (manufactured by Showa Denko Co., Ltd., Karenz MOI), and 224 g of 2-hydroxy-4'-hydroxyethoxy-2-methylpropiophenone

(manufactured by Ciba Specialty Chemicals, Inc., IRG-2959) were placed in a reaction vessel, and 0.76 g of methylhydroquinone was added thereto as a polymerization inhibitor. This mixture was heated to 80°C and stirred for about 26 hours at that temperature. The resulting reaction liquid was dissolved in a mixed solvent of methyl isobutyl ketone and toluene, and the solution was washed with water. Subsequently, methyl isobutyl ketone and toluene were distilled off, and the residue was subjected to recrystallization from ethyl acetate and n-hexane, to thus obtain a photoradical polymerization initiator represented by the formula (1).

Example 1

160 parts by weight of epoxy acrylate of a bisphenol A epoxy resin (manufactured by Dow Chemical Company, DER-332; epoxy equivalent 175 g/eq), 40 parts by weight of DER-332 (manufactured by Dow Chemical Company; epoxy equivalent 175 g/eq) as an epoxy resin, and 10 parts by weight of the photoradical polymerization initiator represented by formula (1) (reaction product of 2-isocyanatoethyl methacrylate and 2-hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methylpropan-1-one) which was obtained in Synthesis Example 1 were heated to dissolve at 90°C, to obtain a resin solution. The solution was cooled to room temperature, and then 8 parts by weight of adipic acid dihydrazide (product name ADH-S; product resulting from further micropulverization using a jet mill of a jet mill-pulverized grade product manufactured by Otsuka Chemical Co., Ltd.), 9 parts by weight of isophthalic acid dihydrazide (product name IDH-S; product resulting from further micropulverization using a jet mill of a jet mill-pulverized grade product manufactured by Otsuka Chemical Co., Ltd.), 25 parts by weight of alumina (manufactured by C.I. Kasei Co., Ltd., SPC-Al, average particle size 1.0 μm), and 5.8 parts by weight of rubber (manufactured by Rohm and Haas Company, Paraloid EXL-2655, average particle size 0.2 to 0.3 μm) were added thereto. The mixture was kneaded with a triple roll mill to obtain a liquid crystal sealing agent according to the present invention. The viscosity (at 25°C) of the liquid crystal sealing agent was 190 Pa·s.

Example 2

To 100 parts by weight of DER-332 (manufactured by Dow Chemical Company; epoxy equivalent 175 g/eq) as an epoxy resin, 20 parts by weight of adipic acid dihydrazide (product name ADH-S; product resulting from further micropulverization using a jet mill of a jet mill-pulverized grade product manufactured by Otsuka Chemical Co., Ltd.), 22.5 parts by weight of isophthalic acid dihydrazide (product name IDH-S; product resulting from further micropulverization using a jet mill of a jet mill-pulverized grade product manufactured by Otsuka Chemical Co., Ltd.), 25 parts by weight of alumina (manufactured by C.I. Kasei Co., Ltd., SPC-Al, average particle size 1.0 μm), and 5.8 parts by weight of rubber (manufactured by Rohm and Haas Company, Paraloid EXL-2655, average particle size 0.2 to 0.3 μm) were added, and the mixture was kneaded with a triple roll mill to obtain a liquid crystal sealing agent according to the present invention. The viscosity (at 25°C) of the liquid crystal sealing agent was 110 Pa·s.

Comparative Example 1

A liquid crystal sealing agent was obtained in the same manner as in Example 1, except that only 8 parts by weight of adipic acid dihydrazide was used as the thermal curing agent, and isophthalic acid dihydrazide was excluded. The viscosity was 160 Pa·s.

Comparative Example 2

A liquid crystal sealing agent was obtained in the same manner as in Example 1, except that only 9 parts by weight of isophthalic acid dihydrazide was used as the thermal curing agent, and adipic acid dihydrazide was excluded. The viscosity was 160 Pa·s.

Comparative Example 3

A liquid crystal sealing agent was obtained in the same manner as in Example 1, except that only 18 parts by weight of adipic acid dihydrazide was used as the thermal curing agent, and isophthalic acid dihydrazide was excluded. The viscosity was 190 Pa·s.

Comparative Example 4

A liquid crystal sealing agent was obtained in the same manner as in Example 1,

except that only 28 parts by weight of salicylic acid hydrazide (manufactured by Otsuka Chemical Co., Ltd.) was used as the thermal curing agent, and adipic acid dihydrazide and isophthalic acid dihydrazide were excluded. The viscosity was 220 Pa·s.

Comparative Example 5

A liquid crystal sealing agent was obtained in the same manner as in Example 2, except that only 20 parts by weight of adipic acid dihydrazide was used as the thermal curing agent, and isophthalic acid dihydrazide was excluded. The viscosity was 50 Pa·s.

Comparative Example 6

A liquid crystal sealing agent was obtained in the same manner as in Example 2, except that only 22.5 parts by weight of isophthalic acid dihydrazide was used as the thermal curing agent, and adipic acid dihydrazide was excluded. The viscosity was 60 Pa·s.

Comparative Example 7

A liquid crystal sealing agent was obtained in the same manner as in Example 2, except that only 40 parts by weight of adipic acid dihydrazide was used as the thermal curing agent, and isophthalic acid dihydrazide was excluded. The viscosity was 60 Pa·s.

Comparative Example 8

A liquid crystal sealing agent was obtained in the same manner as in Example 2, except that only 45 parts by weight of isophthalic acid dihydrazide was used as the thermal curing agent, and adipic acid dihydrazide was excluded. The viscosity was 110 Pa·s.

(i) Liquid crystal contaminability test

0.1 g each of ten sealing agent samples (Examples 1, 2 and Comparative Examples 1, 2, 3, 4, 5, 6, 7, 8) were placed in sample bottles, and were irradiated with 2000 mJ/cm² of ultraviolet radiation to cure. Subsequently, 1 ml of liquid crystal (manufactured by Merck, Ltd., MLC-6866-100) was added to each of the bottles, and the bottles were placed in an oven at 120°C for 1 hour, and then left to stand for 0.5 hours at room temperature. Only the liquid crystals were taken out from the sample bottles

which had been completed with above treatment, and the liquid crystals were introduced into a liquid electrode LE21 (manufactured by Ando Electric Co., Ltd.). The liquid crystal contaminability was evaluated by measuring the specific resistance value of the liquid crystals obtained after 4 minutes at a measurement voltage of 10 V, using an electrometer R-8340 manufactured by Advantest Corporation. The results are presented in Table 1.

(ii) Adhesive strength test

To 100 g of a liquid crystal sealing agent, 1 g of 5 μm thick glass fibers was added as a spacer, and the mixture was subjected to mixing with stirring. This liquid crystal sealing agent was applied on a glass substrate having a size of 50 mm $\times$ 50 mm, and a glass piece having a size of 1.5 mm $\times$ 1.5 mm was overlapped on the liquid crystal sealing agent. In Example 1 and Comparative Examples 1, 2, 3 and 4, the assembly was irradiated with 3000 mJ/cm^2 of ultraviolet radiation using a UV irradiator, and was placed in an oven at 120°C for 1 hour to cure. In Example 2 and Comparative Examples 5, 6, 7 and 8, the assembly was cured by being placed in an oven at 120°C for 1 hour. The adhesive strength was evaluated by measuring the shear adhesive strength of the glass piece using a bond tester manufactured by Seishin Trading Co., Ltd., at a speed of 10 mm per minute. The results are presented in Table 1.

(iii) Moisture resistance reliability test

To 100 g of a liquid crystal sealing agent, 1 g of 5- μm thick glass fibers was added as a spacer, and the mixture was subjected to mixing with stirring. This liquid crystal sealing agent was applied on a glass substrate having a size of 50 mm $\times$ 50 mm, and a glass piece having a size of 1.5 mm $\times$ 1.5 mm was overlapped on the liquid crystal sealing agent. In Example 1 and Comparative Examples 1, 2, 3 and 4, the assembly was irradiated with 3000 mJ/cm^2 of ultraviolet radiation using a UV irradiator, and was placed in an oven at 120°C for 1 hour to cure. In Example 2 and Comparative Examples 5, 6, 7 and 8, the assembly was cured by being placed in an oven at 120°C for 1 hour. Thereafter, the assembly was left to stand for 24 hours under the conditions of a temperature of 121°C, a pressure of 2 atm, and a relative humidity of 100 % using a PCT tester, and then the shear adhesive strength of the glass piece was measured. Thus, the

moisture resistance reliability was evaluated. The results are presented in Table 1.

(iv) Curability test

1 g each of the liquid crystal sealing agents of Examples and Comparative Examples were placed on glass substrates having a size of 50 mm × 50 mm, and were placed in an oven at 120°C for 1 hour to cure. The curability was evaluated by measuring the Shore D hardness. The results are presented in Table 1.

(v) Test on deterioration with time

Approximately 2 g each of the liquid crystal sealing agents of Examples and Comparative Examples were left to stand in a test chamber at a room temperature of 25°C, and the viscosity changes were monitored. The evaluation results of deterioration with time represented by the viscosity increase rate are presented in Table 1.

[Table 1]

	Viscosity	Liquid crystal contaminability (specific resistance value)	Adhesive strength	Moisture resistance reliability (adhesive strength)	Curability	Deterioration with time (viscosity increase rate)
Example 1	190Pa·s	○	○	○	○	○
Example 2	110Pa·s	○	○	○	○	○
Comp. Ex. 1	160Pa·s	○	○	△	×	○
Comp. Ex. 2	160Pa·s	○	○	○	×	○
Comp. Ex. 3	190Pa·s	○	○	○	×	×
Comp. Ex. 4	220Pa·s	○	△	△	○	×
Comp. Ex. 5	50Pa·s	○	○	○	×	○
Comp. Ex. 6	60Pa·s	○	○	○	×	○
Comp. Ex. 7	60Pa·s	○	○	×	○	×
Comp. Ex. 8	110Pa·s	○	○	○	×	○

Remarks) The criteria for evaluation of the respective measurement values

described above are as follows.

Specific resistance value:

- 1.0E+12 or greater
- △ 1.0E+11 to 1.0E+12
- × 1.0E+11 or less

Adhesive strength:

- 60 MPa or greater
- △ 20 MPa to 60 MPa
- × 20 MPa or less

Hardness (Shore D hardness):

- 60 or greater
- △ 20 to 60
- × 20 or less

Viscosity increase rate:

- viscosity increase rate 20 % or less
- △ viscosity increase rate 20 % to 40 %
- × viscosity increase rate 40 % or greater

As shown in Table 1, the fundamental properties required from a liquid crystal sealing agent, that is, liquid crystal contaminability and adhesive strength, are good in Examples as well as in Comparative Examples. However, with regard to the properties of curability, deterioration with time, and moisture resistance reliability, none of the samples of Comparative Examples had the properties in combination, whereas the samples of Examples satisfied all of the properties. Therefore, the liquid crystal sealing agent of the present invention can be said to have low contaminability against liquid crystals throughout the process, have excellent workability in the coating of substrates, excellent stability over time, and excellent moisture resistance reliability.

Industrial Applicability

The liquid crystal sealing agent of the present invention has low contaminability

to liquid crystals, and has excellent workability in the coating of substrates and excellent pot life. The liquid crystal sealing agent is also rapidly curable, and has good pot life, while the cured product has excellent moisture resistance reliability. Therefore, when this sealing agent is used, production of liquid crystal display panels having excellent reliability can be facilitated.

Claims

1. A liquid crystal sealing agent comprising (a) an epoxy resin, (b) an aromatic dihydrazide compound, and (c) an aliphatic dihydrazide compound, and not comprising a monohydrazide compound.
2. The liquid crystal sealing agent according to claim 1, wherein the component (b) isophthalic acid dihydrazide, and the component (c) is adipic acid dihydrazide.
3. The liquid crystal sealing agent according to claim 1 or 2, further comprising (d) a photocurable resin and (e) a photoradical polymerization initiator, in addition to the component (a), component (b) and component (c).
4. The liquid crystal sealing agent according to claim 3, wherein the component (d) is an acrylic resin.
5. The liquid crystal sealing agent according to claim 3 or 4, wherein the component (d) is an epoxy acrylate resin.
6. The liquid crystal sealing agent according to any one of claims 1 to 5, further comprising (f) a silane coupling agent.
7. The liquid crystal sealing agent according to any one of claims 1 to 6, further comprising (g) an inorganic filler having an average particle size of 3 μm or less.
8. The liquid crystal sealing agent according to any one of claims 1 to 7, having a viscosity of 250 Pa·s or less.
9. A liquid crystal display cell sealed with a cured product obtainable by curing the liquid crystal sealing agent according to any one of claims 1 to 8.